

PATENT SPECIFICATION

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(21) Application Nos. 6592/73 (22) Filed 9 Feb. 1973
18609/73 18 April 1973

(23) Complete Specification filed 7 Jan. 1974

(44) Complete Specification published 31 Dec. 1976

(51) INT. CL.² B01J 2/04
C07C 126/08

(52) Index at acceptance

B5A 1C 2A3 2B2

C1A C3CD28 C3CD37 C3CD45 D28 D37 D45 G49

G49D28 G49D37 G50 G50D28 K9B2B K9B2Y

K9B3A K9BY Q4

C2C 20Y 303 30Y 341 34Y 410 412 413 414 41X 578 626

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(72) Inventor FRANK WILLIAM BENNETT

(54) PRILLING



(71) We, FISONS LIMITED, a British Company, of Fison House, 9 Grosvenor Street, London, W.1 do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a process for prilling a molten substance.

It has been common practice to form solid particles from a molten material by allowing droplets of the material to fall down a void tower up which a stream of cooling gas is flowing. However, this process requires the use of a very tall tower if the droplets are to be sufficiently solidified to remain intact upon hitting the base of the tower.

We have now found that if a suspension of drops of a material which volatilises on contact with the molten droplets is caused to flow countercurrent to the molten droplets, then the height of the prilling tower required may be reduced. Surprisingly, little or none of the volatile component is retained by the molten droplets and the product may therefore be produced substantially free from contamination and, where the volatile component is water, not significantly more moist than prills obtained by conventional air prilling techniques, even when the product is not subsequently dried.

Accordingly, the present invention provides a process for prilling a molten material which process comprises causing droplets of the molten material to travel against a countercurrent flow of drops of a material which volatilises on contact with the molten material suspended in a carrier gas stream which is saturated with respect to the volatile material, and collecting the resulting solid skinned droplets.

The process is preferably carried out in a vertical tower by causing the molten

droplets to fall down the tower with the suspension of volatile drops passing up the tower. For convenience, the invention will be described in relation to operation in a vertical tower although it will be appreciated that other orientations may be used, e.g. horizontal injection into a void chamber.

The material which is to be volatilised is a liquid which has a boiling point under the conditions of use which is below the melting point of the molten droplets. Desirably, the volatile material is one with a high latent heat of vapourisation and a high specific heat so that the maximum amount of heat is removed from the molten droplet as it passes through the suspension of drops. The volatile material need not be inert to the molten material, but may comprise an ingredient which it is desirable to incorporate into the solidified droplet, e.g. to enhance its thermal stability or anti-caking properties.

Suitable volatile materials for present use include water and organic liquids, such as a low boiling alcohol, ketone or halogenated hydrocarbon. If desired, the volatile material may be a solution of a substance in water or an organic solvent, the solute being a substance which it is desired to incorporate into the solidified droplet.

The suspension of drops is conveniently formed by spraying the volatile material under pressure with or without a carrier gas into the prilling tower to form a mist or aerosol of drops in the carrier gas which carries the drops up the tower. If need be, supplementary carrier gas may be added separately, although we have found that the spraying operation usually draws sufficient gas into the tower for it to be unnecessary to provide separate means for feeding secondary gas to the tower. A convenient method for forming the suspension of drops in the tower is to spray liquid into the basal

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portion of the tower by means of jets located around the circumference of the tower and directed up the tower. If desired the jets may also be included tangentially to the tower so as to impart a swirl to the suspension formed within the tower.

The gas used to carry or suspend the drops of volatile material in the tower is usually air, although other gases such as nitrogen or carbon dioxide may be used as appropriate.

The material to be prilled may be selected from a wide range of fusible materials. However, the process of the invention is of especial use in the prilling of sulphur and fertilizer materials such as ammonium nitrate, ammonium sulphate nitrate, ammonium phosphate, mixtures of ammonium nitrate with for example mono- or di- ammonium phosphate, potassium chloride or magnesium nitrate, with or without other materials, potassium phosphate, potassium nitrate, sodium nitrate, and mixtures of any of these. The process is most particularly suited to the prilling of molten sulphur, molten urea and molten mixtures of urea. Other materials which may be prilled by the present process include alkali-metal hydroxides. It is usually desired that the molten droplets contain an initial water content of not more than 10% by weight.

In the process of the invention, droplets of the molten material are formed in any convenient manner, e.g. by the use of a spinning basket prilling head, by spraying the molten material, or allowing the molten material to flow through a plurality of fine apertures in the base of a rainmaker prilling head, to form droplets of the desired size range, eg from 0.5 to 4 mms. The droplets then fall through a zone containing drops of volatile material suspended in a gas stream flowing countercurrent to the falling molten droplets. As they fall through the suspension, the molten droplets collide with the drops of the volatile material and heat is removed from the molten material. It is therefore desirable to ensure that the maximum number of collisions between the molten material droplets and the volatile drops take place. This may be achieved by injecting volatile material into the tower at a high rate. However, the upper limit of rate of injection of the volatile material is dictated by the load of suspended droplets which the gas stream flowing up the tower can carry. Whilst the load carried by the gas stream can be increased by increasing the linear flow rate of the gas up the tower, the linear flow rate must not exceed the terminal velocity of the molten droplets being prilled into the tower. We therefore prefer to use linear gas flow rates in the tower of not more than 10 metres per

second. On the other hand, high gas flow rates require expensive pumping installations and from an economic standpoint it is preferred to use low linear gas flow rates. However, a minimum flow rate is set by the terminal velocity of the drops of the volatile material which velocity must be equalled or exceeded if the drops are to be suspended in the gas stream. We therefore prefer to use linear gas flow rates of more than 0.1 metres per second in the tower. Whilst it will be appreciated that the loading of the gas stream and its velocity can be varied to suit a given case, it is essential that the gas stream be saturated with respect to the volatile material in order that drops of the volatile material may exist. This saturation requirement applies to that part of the tower in which the suspension of drops is to flow and need not hold true for other parts of the tower. In practice it is sufficient to ensure that sufficient volatile material is injected into the tower to supersaturate the total volume of gas being injected into the tower. Whilst the dew point of the gas stream may vary with temperature, we have found that local fluctuations in temperature within the tower do not significantly affect successful operation of the process and for the purposes of this invention, saturation denotes the overall notional state of the gas when at the temperature at which it leaves the tower.

Whilst it would be thought desirable to achieve total cooling and solidification of the molten droplets as they pass through the suspension of volatile drops, this is usually not necessary in that droplets which have been solidified to 60% or less by weight are usually sufficiently strong to be subjected to conventional handling and processing techniques. Furthermore, the residual heat in the partially solidified droplets aids removal of any volatile material remaining thereon and it may be possible to dispense with the need to dry the solidified droplets.

The residence time of the molten droplets in the suspension of volatile drops will also affect the extent of solidification. It will usually be preferred to limit the height of the suspension zone in the tower to less than 15 metres, e.g. 2 to 10 metres. It is also preferred that the suspension zone does not extend right up to the means by which the molten droplets are formed and it is usually desirable to remove the gas stream 0.4 to 2 metres below the means so as to leave a clear zone at the top of the tower. It is also preferred that the suspension zone does not extend right to the base of the tower in order that at least some of the excess volatile material which may remain on the surface of the partially solidified molten droplets is evaporated off by

the residual heat still retained by the partially solidified molten droplet. To this end it will usually be desired to inject the volatile material some way up the tower so as to leave a clear zone, e.g. 1 to 8 metres deep, below the suspension zone.

In view of the inter-relationships outlined above it is not possible to give concise conditions under which the prilling tower should be operated. However, in general: the molten droplets will have an initial temperature just above, e.g. 2-10°C above, their solidification temperature (although temperatures as much as 40°C above the solidification point may be used in the case of sulphur and high melting materials); the molten droplets will be approximately the same size as that desired for the final product; the depth of the zone in the tower in which the suspension flows and the amount of volatile material carried by the gas stream are such that at least 10%, preferably about 30%, of each molten droplet solidifies as it passes through the suspension of volatile drops; the drops of volatile material injected into the tower will have an initial average size in the range 1 to 500, e.g. 20-100, micrometres (although it will be appreciated that the drops may change in size in the tower); and the gas flow rate will be between 0.10 to 10, preferably 0.45 to 6, metres per second.

After they have fallen through the suspension of drops, the molten droplets will be partially or wholly solidified as indicated above. These droplets are recovered from the prilling tower by any suitable method and may be given a further cooling and/or drying treatment if desired, although it may prove possible in some cases to achieve adequate drying in the clear zone below the suspension zone.

In a particularly preferred form of the process of the invention a cushion, into which the partially solidified droplets fall and are cooled further before being removed, is formed below the suspension of drops. By providing the cushion, the height of the prilling tower may be yet further reduced. The cushion may take a number of forms. Thus, it may be a fluidised bed of solid particles fluidised either by the gas stream which is to carry the drops of volatile material or by a separate gas stream. The bed may be composed of the solidified droplets or of some other material, notably one with which the solidified droplet is to be coated or impregnated. By controlling the conditions above the fluidised bed, the adhesive properties of the surface of the molten droplets may be modified thus controlling the amount of bed particles picked up by the droplet during its residence in the bed. In order to improve the cooling effect of the bed, cooling heat exchanger

surfaces, e.g. coiled pipes, may be immersed in the bed.

The fluidised bed may be formed from a wide range of materials of any suitable size, e.g. of less than about 200 mesh BSS. Examples of suitable materials include the material being prilled; limestone; sand; mica; gypsum; bentonite; montmorillonite; attapulgite; kieselghur; talc; fertilizer materials, such as potassium and ammonium salts of phosphoric, sulphuric or nitric acids, potassium chloride and potassium metaphosphate; magnesium and aluminum salts or compounds, such as the oxides, nitrate or carbonates thereof and hydrates thereof; basic slag; phosphate rock; cements; clays and earths. Mixtures of materials may be used if desired.

Alternatively, the cushion may be a pool of a liquid into which the droplets fall. This liquid may be the same as the volatile material in the suspension of drops or may be different. Thus, the liquid could be a mineral oil of the type commonly used to coat fertilizer granules or it could be a solvent material to remove excess volatile material picked up by the molten droplets as they passed through the suspension of drops. The liquid may be cooled in order to ensure more rapid solidification of the droplets.

It is preferred that the cushion lie some distance e.g. 1 to 8 metres below the suspension zone in the tower in order that volatile material may be evaporated from the droplets before they enter the cushion.

The invention will now be illustrated in the following Examples in which all parts and percentages are by weight:

Example 1

Molten ammonium nitrate at 171°C was prilled down a glass column 4.5 metres high and 7.5 cms internal diameter at a rate of 3 kgs per hour. Air was blown at a rate of 0.67 metres/sec up the tower through a bed of commercial fullers' earth of particle size 2 to 50 micrometres. This formed a fluidised bed of particles whose upper surface was about 3.5 metres below the point of entry of the molten ammonium nitrate droplets. A fine spray of water (mean drop size 100 micrometres approximately) was introduced at the rate of 8 mls/second into the column just above the fluidised bed in a carrier stream of air. The product was a spherical prill, average size 2.5 mms which carried 1.1% of fullers' earth. When no water was sprayed into the tower, the product was poorly shaped and carried 4.26% of fullers earth. It was necessary to increase the distance between the point of entry of the molten droplets and the top surface of the fluidised bed to 5.5 metres before an acceptable shaped product was obtained, and this still carried 4% of the

fullers' earth.

Example 2

Molten sulphur at a temperature of 120°C was prilled down a column 4.5 metres high and 7.6 cm internal diameter at a rate of 3 kgs/hour. Water was injected up the column with two pneumatic atomising nozzles, placed 2.4 metres from the top of the column. The spray nozzles delivered a total of 0.45 l/min of water and 2.8 l/min of air and produced drops of approximately 100 micrometre mean diameter. The spray nozzles drew additional air at 20°C into the column so that the total air velocity, as measured at the top of the column, was about 6.0 metres/second. The mist travelled up the column for a distance of 2.0 metres before being lead out below the prilling nozzles. The sulphur droplets fell through the mist and then through 2.1 metres of mist free space below the mist to give solid prills 1-2 mm in diameter at the base of the column.

25 WHAT WE CLAIM IS:

1. A process for prilling a molten material which process comprises causing droplets of the molten material to travel against a countercurrent flow of drops of a material which volatilises upon contact with the molten material suspended in a gas stream which is saturated with respect to the volatile material; and collecting the resulting solid skinned droplets.
2. A process as claimed in claim 1 wherein the droplets of molten material fall down a tower.
3. A process as claimed in either of claims 1 or 2 wherein the volatile material is water.
4. A process as claimed in any of the preceding claims wherein the molten material is sulphur.
5. A process as claimed in any of claims 1 to 4 wherein the molten material is a fertilizer material.
6. A process as claimed in any of the preceding claims wherein the suspension of

drops of volatile material is carried in a stream of air.

7. A process as claimed in any of the preceding claims wherein from 10 to 30% by weight of the molten droplet solidifies as it passes through the suspension of drops of volatile material.

8. A process as claimed in any of the preceding claims wherein the suspension of drops of volatile material is carried by a gas stream flowing at a linear velocity of from 0.1 to 10 metres per second.

9. A process as claimed in any of the preceding claims wherein the molten droplets fall through a zone 0.4 to 2 metres deep which is substantially free from drops of volatile material, then through a zone 2 to 10 metres deep containing the suspension of drops of volatile material and then through a zone 1 to 8 metres deep which is substantially free from drops of volatile material.

10. A process as claimed in any of the preceding claims wherein the solidified or partially solidified molten droplets fall into a recipient cushion.

11. A process as claimed in any of the preceding claims wherein the cushion is provided by a fluidised bed of particles.

12. A process as claimed in any of claims 1 to 10 wherein the cushion is provided by a pool of liquid.

13. A process according to claim 1 substantially as hereinbefore described.

14. A process according to claim 1 substantially as hereinbefore described in the Examples.

15. A solid particle whenever produced by a process as claimed in any of the preceding claims.

T. I. P. DUMMETT,
Chartered Patent Agent,
Agent for the Applicants,
Fisons Limited,
Fison House,
Princes Street,
Ipswich,
Suffolk.